



## THE REDUCTION OF ALUMINA CONSIDERED FROM A THERMO-CHEMICAL STANDPOINT.\*

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The writer is a firm believer in the usefulness of thermochemical data as a guide in chemical experiment. However, the deductions drawn from these data are often incorrect, because all the conditions have not been taken into account. Berthelot has postulated the "law of maximum work," which affirms that every chemical reaction takes place with the maximum production of heat possible by the combination of the reacting substances. This law, however, is too limited; it leaves out of consideration altogether the disturbing effect of the relative masses of the substances, their physical condition and the physical condition of the products. For instance, an excess of a reducing agent is often necessary to reduce an oxide, producing or causing to take place a highly endothermic reaction. Again, if one of the possible products of a reaction would be in such a physical condition as to be quickly and completely removed from the sphere of the reacting bodies, its formation will be greatly accelerated. If two solutions are mixed and one of the possible products of their reaction is *insoluble* in the solution, this fact will determine the formation of that substance, even though the reaction is an endothermic one. The heat deficit will simply be made up by an abstraction of heat from the solution; it will be cooled. Similarly, if two solids or liquids, or a solid and a liquid, are brought into intimate contact, and the possible result of their reaction should be a gas, the reaction will tend to take place, even if endothermic, because the gas escapes from the field of reaction as soon as produced, and so the inverse reaction is prevented. In such a case, putting pressure on the substances would hinder the formation of gas and retard the

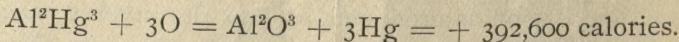
\* Read before the Chemical Section, February 19, 1895.

reaction ; removing the pressure would facilitate the reaction. It has been proved, experimentally, that mercuric oxide and carbon react at a lower temperature when warmed in a vacuum than when at ordinary pressure.

Another important point is, that there is, under a given pressure, a critical point of temperature at which reactions first take place, the explanation of which is that the particles of the original substances are themselves bound together by chemical affinity, and that the molecular vibration corresponding to a certain temperature is necessary before the new affinities tending to produce the reaction can overcome the original affinities of the primary substances. At 555° C. the atoms of oxygen and hydrogen, in the molecules of their respective gases, are vibrating to such distances from their mutual centre of attraction, that the new affinity of the unlike atoms for each other is able to disrupt the original molecules, and combination occurs. Similarly, carbonic oxide can break up the oxygen molecule only at 655° C. These remarks apply to the free gases at ordinary pressure. Under other conditions, the oxidation can go on at different temperatures.

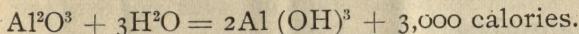
If the substances are brought to the critical temperature at which they react, and the reaction at that temperature is exothermic, then the exchange will take place and proceed of itself until complete. If the reaction is endothermic, the first reacting portions absorb heat from the rest and lower the temperature below the critical point, thus putting a stop to the reaction, the exchange starts again only when the temperature is kept up to the critical point by the liberal supply of heat from without. This is the *modus operandi* of the reduction of many strong oxides.

The heat of formation of a molecular weight of alumina (102 parts) was determined by Baille and Féry, by oxidizing aluminium amalgam. The reaction is



This is evidently the heat of oxidation of liquid aluminium to solid alumina, *minus* the heat of formation of  $\text{Al}^2\text{Hg}^3$ . This latter quantity is unknown, but is probably quite

small. These investigators determined the heat of hydration of alumina; thus



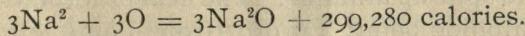
Berthelot, long previously, had found the heat of formation of hydrated alumina to be 391,600 calories. This would give 388,600 for anhydrous alumina, but this figure is based on the oxidation of *solid* aluminium. To compare it with Baille and Féry's figures, we must *add* to it the latent heat of aluminium at 0° C., which is calculated as follows:

	Calories.
Latent heat of 1 kilo aluminium at the melting point	100.0
Heat given out by 1 kilo of molten aluminium in falling from 625° to 0° = $625 \times 0.308$ (sp. heat molten aluminium), determined by Pionchon	<i>Cal.</i> 192.5
Heat given out by 1 kilo of solid aluminium through the same range (writer's experiments)	158.3
Decrease in the latent heat	34.2
Latent heat of 1 kilo at 0° C.	65.8

The latent heat of 54 kilos (Al<sup>2</sup>) is, therefore, . . . . . 3550.0

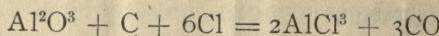
Adding this to Berthelot's corrected value for anhydrous alumina from solid aluminium, the sum is 392,150 calories. This agrees so closely with Baille and Féry's figures that the latter are accepted as being very near the truth.

Concerning the reduction of this compound to metallic aluminium, two ways are possible—the direct and the indirect. By the first I mean the use of an agent which is powerful enough to reduce it to metal at a single step; by the indirect is meant, first, reducing alumina to a more tractable aluminium compound, and then reducing the latter. Leaving electricity entirely out of consideration, there are but very few reducing agents which can decompose alumina directly, and they only at very high temperatures. Sodium does not act on it at any temperature, since sodium oxide is a far weaker compound than alumina.



If the alumina, however, is converted into an oxygen-free aluminium salt, its affinities are then much weaker, while the reducing power of sodium is relatively much greater.

Chlorine and carbon together decompose alumina,



Heat absorbed:

Decomposing alumina . . . . . 392,600

Heat liberated:

Aluminium chloride . . . . . 325,510

Carbonic oxide . . . . . 88,200

———— 413,710

Excess of heat . . . . . 21,110

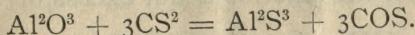
This reaction proceeds easily at a bright red heat; in fact, we not only have an exothermic reaction, but the products also are all gaseous, and as soon as the critical temperature at which the reaction begins is reached, the operation proceeds rapidly and completely.

The aluminium chloride is easily reduced by sodium, potassium, lithium and magnesium, perhaps to a slight degree by manganese and zinc, which have about an equal affinity for chlorine. No other substances, organic or inorganic, besides these few rare alkaline and alkaline-earth metals, have a heat of combination with chlorine sufficient to decompose aluminium chloride.

Bromine and iodine vapors do not act like chlorine, and the reason is seen in casting up the thermal data. The difference between the heat of formation of alumina and three molecules of carbonic oxide is  $392,600 - 88,200 = 304,400$  calories. Against this, chlorine formed aluminium chloride and gave 325,510 calories, making the reaction exothermic by 21,110 calories. Bromine, however, in forming the bromide, gives only 243,550 calories, leaving a deficit of 60,850 calories, while iodine gives only 144,310, leaving a deficit of 160,190 calories. The only known way of making these compounds is directly from aluminium itself.

Sulphur, also, is unable either alone, or with the assistance of carbon, to split up alumina. The heat of formation of aluminium sulphide being 127,950 (from liquid aluminium), the enormous deficit of  $304,400 - 127,950 = 176,450$  calories, makes the reaction impracticable. However, when carbon bisulphide vapor is passed over white-hot alumina, alu-

minium sulphide is formed. It would appear at first sight as if the compound of carbon and sulphur would be less likely to produce the reaction than those elements uncombined; but the secret of this paradox is disclosed when we note that carbon bisulphide is one of the few endothermic compounds, absorbing 29,000 calories in its formation, and giving out just that amount in its decomposition. This helps to reduce the deficit by just so much. Further, carbonic oxide is not formed, but carbonyl sulphide, which has a heat of formation 4,700 calories higher for each atom of oxygen taken up. Casting up the thermal data, we have



Heat absorbed :

	<i>Calories.</i>
Decomposing alumina . . . . .	392,600

Heat evolved :

Formation of aluminium sulphide . . . . .	127,950
"    " carbonyl sulphide . . . . .	102,300
Decomposition of carbon bisulphide . . . . .	87,000
	317,250

Heat deficit . . . . .	75,350
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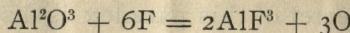
This is still a large deficiency, but the critical temperature for the reaction is a white heat, and, if the supply of carbon bisulphide is abundant and the heating is kept up energetically, the reaction is practicable.

As for reducing this sulphide to metal, thermal data show us that only the alkaline and alkaline-earth metals can accomplish it easily, while manganese, zinc, tin, iron and copper can do it to a small extent when used in large excess, making use of the influence of mass to bring about the endothermic reaction. This compound recommends itself more particularly for electrolytic decomposition. When mixed with an alkaline sulphide it forms an easily fusible double sulphide, which theoretically requires less than one volt to decompose it.

Alumina is easily converted into its fluoride, which, however, can only be decomposed chemically by the alkaline or

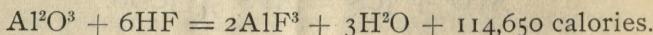
alkaline-earth metals. Even fluorine alone acts energetically on it, raising it to incandescence.

The reaction



sets free  $555,550 - 392,600 = 162,950$  calories, which accounts for the phenomena observed.

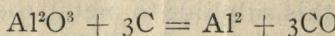
Even hydrofluoric acid gas can be used for the reaction, the splitting up of six molecules of gaseous hydrofluoric acid requiring, at  $0^\circ\text{ C.}$ , 222,600 calories, against which we have the formation of three molecules of water, 174,300 calories, leaving for the reaction a net excess of



A reaction similar to this is impracticable with hydrochloric acid gas, and we find that it would be endothermic to the extent of about 30,000 calories.

#### DIRECT REDUCTION.

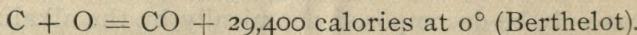
Minet has measured carefully the voltage required to decompose alumina dissolved in a fluoride bath, using a carbon anode, at which carbonic oxide is formed. As one volt represents a thermal value of 23,000 calories for each equivalent of oxygen liberated, it would represent  $23,000 \times 6 = 138,000$  calories for each molecule of alumina split up. The number of calories represents, therefore, the thermal value of the following reaction :



at the temperatures given. Minet's best experiments gave:

Temperature.	Voltage.	Calorific Equivalent ( $30^\circ$ )
900°	2'40	331,000
1100°	2'17	299,460

If we can add to these numbers the heat evolved by the reaction  $3\text{C} + 3\text{O} = 3\text{CO}$ , at these temperatures, we shall obtain the value of the reaction  $\text{Al}^2 + \text{O}^3$ , or the heat of oxidation of liquid aluminium to liquid alumina. This calculation is made as follows :



$$\text{Specific heat of carbon (}t > 900^\circ\text{)} \dots \dots \dots 0.53 \times \frac{134.6}{t} \quad (a)$$

(Pionchon.)

$$\text{Specific heat of oxygen} \dots \dots \dots 0.2114 + 0.00001875t \quad (b)$$

(LeChatelier and Mallard.)

$$\text{Specific heat of carbonic oxide} \dots \dots \dots 0.245 + 0.0006t \quad (c)$$

(Regnault.)

Therefore,

$$C + O \left( \begin{matrix} \text{at } t^\circ \\ t > 900^\circ \end{matrix} \right) = 29,400 + (12a + 16b - 28c)t. \\ = 27,785 + 2.8824t - 0.0003t^2.$$

Substituting, we have

$$\text{At } 900^\circ, C + O = 30,136 \quad 3(C + O) = 99,408$$

$$\text{At } 1100^\circ, C + O = 30,592 \quad 3(C + O) = 91,776$$

Adding these to the values of the reaction given by Minet's experiments, we have

$$\text{At } 900^\circ Al^2 + O^3 = 331,000 + 90,408 = 421,408 \text{ cal.}$$

$$\text{At } 1100^\circ Al^2 + O^3 = 299,460 + 91,776 = 391,236 \text{ cal.}$$

Now, we know that at  $0^\circ$ ,  $Al^2 + O^3 = 391,600$  calories, the only difference between this and the figures just derived being that the latter is calculated for *solid* alumina. For liquid alumina, we should have to subtract from it the latent heat of fusion of alumina. This is not known, but if we estimate it at forty-three calories per kilo (from analogy with other oxides), we may subtract  $43 \times 102 = 4,400$  calories. We then have the heat of formation of liquid alumina from liquid aluminium, as follows;

	Calories.
$0^\circ$ . . . . .	387,200
$900^\circ$ . . . . .	421,408
$1100^\circ$ . . . . .	391,236

It will be noticed that the value has reached a maximum between  $0^\circ$  and  $900^\circ$ , and is rapidly decreasing; in other words, above  $1,000^\circ$  alumina rapidly becomes easier to decompose. A curve passing through the above values would be of the following form:

$$Q = 387,200 + 192.6t - 0.1716t^2.$$

The question now is: "At what temperature would the heat of oxidation of our reducing agents equal the heat of formation of alumina? We may fairly assume that if that

point is above the critical point for the reaction, reduction will there begin.

*Carbon.*—The formula for the heat of oxidation of carbon to carbonic oxide has already been deduced. We therefore have

$$\begin{aligned} \text{Al}^2 + \text{O}^3 &= 387,200 + 192.6t - 0.1716t^2 \\ 3(\text{C} + \text{O}) &= 83,355 + 8.6472t - 0.0009t^2 \end{aligned}$$

When these two expressions become equal to each other

$$t = \underline{\underline{1980^\circ}}$$

If liquid carbon is the reducing agent, its efficacy is about 21,000 calories greater than solid carbon, and

$$t = \underline{\underline{1940^\circ}}$$

As verifying these calculations, I may refer to the fact that liquid alumina is, beyond a doubt, reduced by carbon in electric furnaces, because the output of aluminium is greater than the number of ampères passing through the furnace could theoretically produce, and, also, because decomposition can be produced by a rapidly-alternating current, where electrolysis is out of question. The temperature in such furnaces is probably about  $3,000^\circ$ . Again, in a Pennsylvania iron blast furnace, in which the temperature is almost certainly not over  $2,000^\circ$ , as much as one per cent. of aluminium has been reduced into the iron. The liquid carbon in the iron in the crucible is here the reducing agent, reducing aluminium from a slag carrying as high as twenty-five per cent. of alumina.

It thus appears that both calculation and practice unite in showing that carbon begins to reduce alumina in the neighborhood of  $2,000^\circ$  C.

#### *Hydrogen.*—

$$\begin{aligned} \text{H}^2 + \text{O} &= 69,000 \text{ calories (to liquid H}_2\text{O at } 0^\circ) \\ &= 58,100 \quad " \quad (\text{to vapor of water at } 0^\circ) \end{aligned}$$

$$\text{Specific heat of hydrogen} = 3.3820 + 0.0003t \quad (a)$$

$$\text{“ “ “ oxygen} = 0.2214 + 0.00001875t \quad (b)$$

$$\text{“ “ “ water vapor} = 0.4208 + 0.0000182t \quad (c)$$

$$\begin{aligned} \text{H}^2 + \text{O (at } t^\circ) &= 58,100 + (2a + 16b - 18c)t \\ &= 58,100 + 5.9544t - 0.001712t^2 \end{aligned}$$

We therefore have

$$\begin{aligned} \text{Al}^2 + \text{O}^3 &= 387,200 + 192.6t - 0.1716t^2 \\ 3(\text{H}^2 + \text{O}) &= 174,300 + 17.863t - 0.0051t^2 \end{aligned}$$

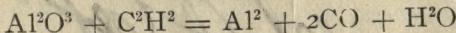
When these two expressions become equal to each other,

$$t = \underline{\underline{1770^\circ}}$$

This is just about the melting point of platinum, and may appear lower than can possibly be the fact; nevertheless, Mr. H. Warren, in England, has recently succeeded in reducing alumina to aluminium in a current of hydrogen gas, the alumina being inside a lime tube heated on the outside by the oxyhydrogen flame. It is hardly possible that the temperature inside the tube could have exceeded  $2,000^\circ$ ; yet complete reduction to metallic globules was obtained.

This second confirmation of the calculations by experiment induces me to add, in conclusion, the following observations:

Acetylene gas,  $\text{C}^2\text{H}^2$ , has a negative heat of formation of 51,500 calories. It is, therefore, just by that much a more powerful reducing agent than  $\text{C}^2$  and  $\text{H}^2$  alone. The equation is :



The thermal equations are :

$$\begin{aligned} \text{Al}^2 + \text{O}^3 &= 387,200 + 196.2t - 0.1716t^2 & (a) \\ 2(\text{C} + \text{O}) &= 55,570 + 5.7648t - 0.0005t^2 & (b) \\ \text{H}^2 + \text{O} &= 58,100 + 6.7640t - 0.0006t^2 & (c) \\ \text{C}^2 - \text{H}^2 &= 51,500 & (d) \end{aligned}$$

making  $b + c + d = a$

$$t = \underline{\underline{1870^\circ}}$$

I am inclined to think that this highly endothermic compound would reduce alumina at an even lower temperature than this, because we have not only the benefit of its great heat of decomposition, but we also have, at the moment when it decomposes, the carbon and hydrogen atoms *in statu nascendi*, and we thus have all the advantages of a nascent reducing agent. I need not, to an audience of chem-

ists, expatiate on the greater chemical activity of a nascent reducing agent.

The recent developments in the manufacture of calcium carbide and acetylene open up a possibility in the way of reducing alumina which may bear fruit. Allow me, at least, to claim for thermo-chemistry, rightly understood, that it is a most helpful guide to intelligent experiment.

LEHIGH UNIVERSITY, Bethlehem, Pa., February 19, 1895.



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